Preliminary Results of a Geochemical Investigation of Halogen and Other Volatile Compounds Related to Mineralization, Part 1: Lara Volcanogenic Massive-Sulphide Deposit, Vancouver Island (NTS 092B/13)

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Introduction

The halogens (F, Cl, Br and I) are common constituents of igneous, metamorphic and sedimentary rocks (Billings and Williams, 1967). They are particularly enriched in differentiated magmas; the hydrothermal fluids and volatile compounds derived from them play an important role in the mobilization and transport of metals in ore-forming systems. In the primary environment, they reside in a variety of hydrous minerals, including micas, amphiboles, scapolite, topaz and apatite. High halogen concentrations are also documented in high-salinity liquid phases or in tiny secondary-mineral phases in fluid inclusions in igneous and hydrothermal minerals (Kendrick et al., 2012; Kendrick and Burnard, 2013). In the hydrothermal environment, halogens can be concentrated in alteration minerals such as micas, clays and topaz, and the gangue mineral fluorite. On exposure to surface conditions, these minerals weather and release their halogens as volatile gases (Br and I) and/or their more stable compounds, or water soluble ions (F and Cl) that disperse to form detectable anomalies in the surficial environment (Trofimov and Rychkov, 2004).

In mineral exploration there are case histories that demonstrate positive responses for all these elements and compounds over zones of concealed mineralization (Al Ajely et al., 1985; Ridgway, 1989, 1991; Ridgway et al., 1990; Trofimov and Rychkov, 2004). However, these methods have seen little or no application to the exploration for minerals in the extensively overburden-covered terrains of British Columbia (BC).

In 2005, Geoscience BC sponsored a project entitled 'Halogens in surface exploration geochemistry: evaluation and development of methods for detecting buried mineral deposits' (Dunn et al., 2007). This initial study investigated the optimal analytical procedures available at the time for determining halogen concentrations in soil and vegetation, and provided new halogen data from the Mount Polley, QR and 3Ts deposits. A recommendation from this study was that, since a clear response of labile halogens in soils and vegetation over known mineralization had been established, targets concealed by overburden (both Quaternary and volcanic) needed to be tested and analytical methodology needed to be refined. Bissig et al. (2013), as part of a wider study looking at geochemical responses of blind Cu-Au porphyry–style mineralization beneath Chilcotin basalt cover at the Woodjam property (near the community of Horsefly, central BC), demonstrated that the partial-extraction techniques Bioleach and Enzyme Leach[SM] produced robust Br and I anomalies over blind mineralization at the Three Firs prospect.

The current project expands on the 2005 study. It aims to further investigate responses of halogen and other volatile compounds (not included in the 2005 study) in organic media over blind and thinly covered mineralization. Two study sites, both on Vancouver Island, have been selected for this investigation: Lara is a volcanogenic massive-sulphide (VMS) target that is buried by 5–10 m of glacial till; Mount Washington is an epithermal system with a thin veneer of overburden. This paper summarizes the field program and objectives of the first of these—Lara. A second paper in this volume outlines the approach at Mt. Washington (Heberlein and Dunn, 2017). Objectives of this study are to broaden the range of sample media tested and to look at the effectiveness of commercially available analytical methods and new instrumentation (some not available in 2005) for detecting mineralization-related halogen and volatile-compound responses.

This project aims to test the geochemical responses of halogens and other mineralization-related compounds (e.g., NH_4, PO_4 and SO_4) in a variety of organic media, including 1) soil Ah horizon, 2) foliage from the most prevalent tree species, and 3) foliage from selected understorey species. Volatile-element distributions are to be compared with

Keywords: *British Columbia, deep-penetrating geochemistry, Lara, base metals, biogeochemistry, halogens, western hemlock, salal, Oregon grape, sword fern, Ah horizon, oxyanions, ammonium, nitrate, nitrite, sulphate, phosphate, Bioleach*

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commodity- and pathfinder-element signatures for the same media.

An ongoing geochemistry-research project of the Mineral Deposit Research Unit (MDRU) at The University of British Columbia is investigating the processes and controls of labile-element mobility. That project aims to develop a process-based model of trace-element dispersion in the surface environment above concealed massive-sulphide mineralization, and provides a useful context and backdrop to this study.

Relevance to the Exploration Community

This study is designed to provide the mineral-exploration community with an understanding of the potential advantages of determining volatile components, derived from zones of VMS and epithermal Au mineralization, that accumulate in surface soils and common coniferous trees and shrubs in regions with glacial-sediment cover. It assesses the relative capabilities of each medium for preserving the secondary geochemical-dispersion patterns related to a blind mineral deposit. The study assesses the value to the exploration community of an alternative analytical approach for geochemical-sampling programs in areas where conventional soil-sampling methods are found to be ineffective and/or where contamination from mining activities might present a problem for the use of other geochemical-exploration sampling media.

Study Area

The test site at the Lara VMS deposit (Coronation zone), located near Chemainus, is readily accessible by a good road network, thus minimizing the logistical costs required for the field component of the study (Figure 1).

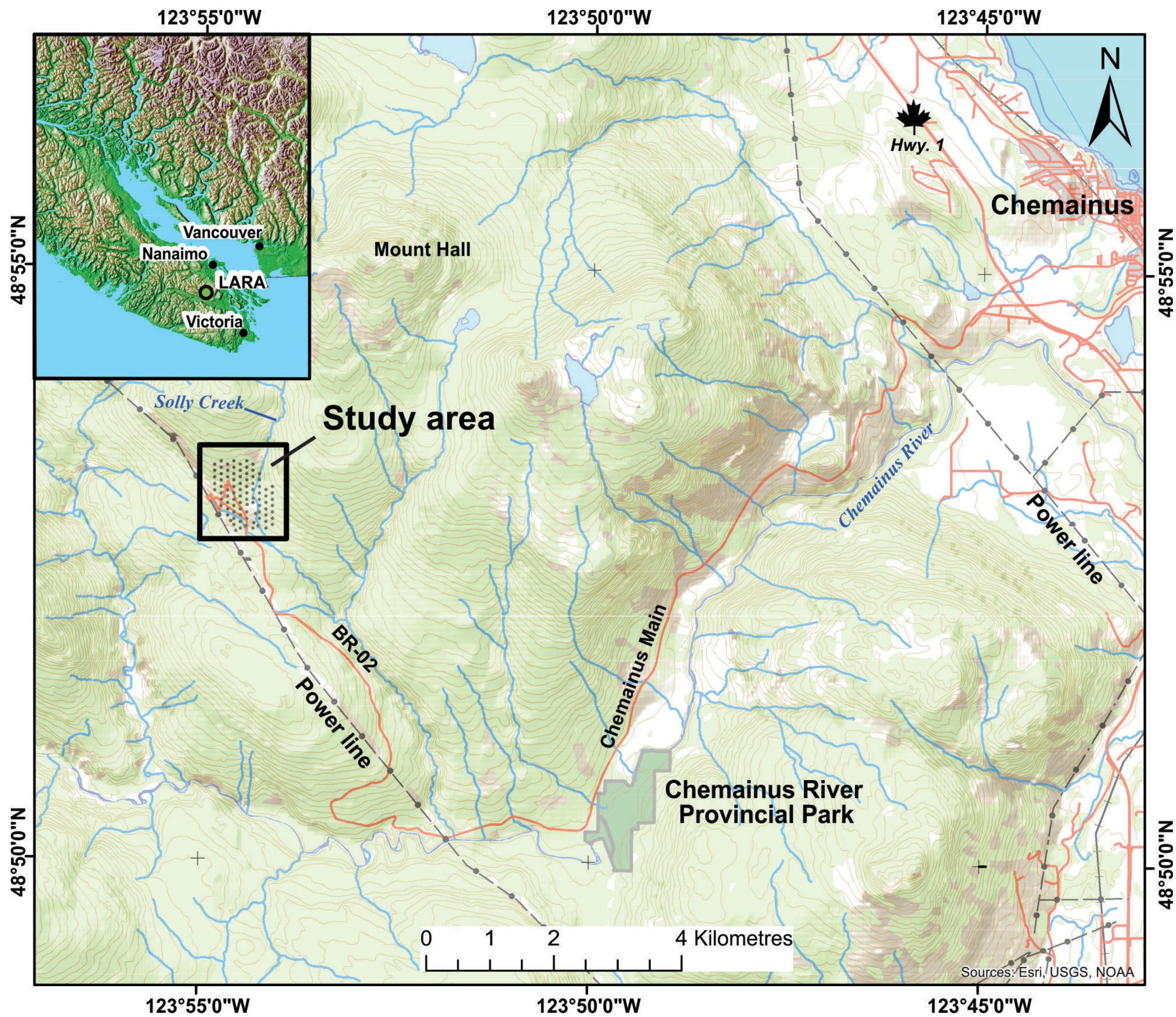

Figure 1. Location of the Lara study area (grey box), east-central Vancouver Island, showing sample stations. Contains information licensed under the Open Government Licence – Canada.

Location and Access

The Lara deposit ('Lara') lies in the Victoria Mining Division of southern Vancouver Island, some 75 km north of Victoria, 15 km northwest of Duncan and 25 km west-southwest of Chemainus, which was the logistical base for the field portion of the study. Access to the project area is via the active Chemainus Main logging road to Kilometre 19 and then the BR-02 Mount Brenton Forest Service Road to Kilometre 7.5. From there, a network of secondary logging roads, drilling roads and a BC Hydro right-of-way provide access to parts of the sampling area.

Surficial Environment

Lara is located at the boundary between the Vancouver Island Ranges to the north and west, and the Nanaimo Lowlands to the south and east (Holland, 1976), in an area of rolling topography. The study site lies on the lower southern slopes of Coronation Mountain and Mount Hall, between elevations of 610 and 770 m (Figure 2). Solly Creek is the main drainage separating the two peaks. It crosses the study area from north to south before turning southeastward to drain into the Chemainus River.

The entire project area was logged in the 1950s. Consequently, the present-day vegetation consists of mixed second-growth forest comprising mostly western redcedar (*Thuja plicata*), western hemlock (*Tsuga heterophylla*) and Douglas-fir (*Pseudotsuga menziesii*). Other species present include western white pine (*Pinus monticola*), paper birch (*Betula papyrifera*) and red alder (*Alnus rubra*). Understorey species vary considerably from place to place. Western sword fern (*Polystichum munitum*) is common in moist coniferous forests at low elevations. It grows best in a well-drained acidic soil of rich humus. Salal (*Gaultheria shallon*), a leathery-leaved shrub in the heather family, is tolerant of both sunny and shady conditions at low to moderate elevations. It is a common coniferous-forest understorey species and may dominate large areas and form dense, nearly impenetrable thickets. Oregon-grape (*Mahonia sp.*) has holly-like leaves and prefers the more canopied areas.

There are no published surficial-geology maps for the immediate Lara area, only the area to the east where the general ice-flow direction is indicated (Blyth and Rutter, 1993). The distribution of surficial materials shown in Figure 2 has been interpreted primarily from field observations and aerial photographs. Regolith mapping, undertaken by M. Bodnar for his M.Sc. thesis at MDRU, is incorporated into this interpretation.

Figure 2 shows that the northern two-thirds of the project area are underlain by a veneer or blanket of glacial till (dark green; Figure 2). This is interpreted to be a basal or lodgment till; it is exposed in roadcuts, stream banks, trenches and the large opencut adjacent to the Coronation zone underground portal. Although its thickness is difficult to estimate from present-day exposures, drilling and trenching records show that it varies between <1 m and >50 m (Kapusta, 1990; Archibald, 1999). The presence of outcrops and bedrock-derived colluvium within the till-covered area (Figure 2, reddish brown and brown units) suggest that there is a well-developed buried bedrock topography. In general, there is a gradual thinning of the till deposits upslope.

Recent mapping by M. Bodnar (pers. comm., 2016) has augmented the interpretation of the surficial geology in the central part of the study area. Alluvial deposits, consisting of coarse sand, gravel and channel conglomerate (Figure 2, pale green unit), define a paleochannel system that is now occupied by Solly Creek. First-order tributaries show evidence of erosional recession to the northwest, with backscarps incised into and causing reworking of the till blanket. A recent landslide in the northernmost tributary on Figure 2 has delivered large amounts of unsorted sediment into Solly Creek. The apparently rapid incision of the drainage system has caused it to dissect its own alluvial deposits. Remnants of older alluvial terraces occur along the hillside to the west of Solly Creek between elevations of 660 and 675 m (Figure 2, pale yellow unit). These deposits define the upper edge of a 200 m wide alluvial sand and gravel plain bordering the present-day creek and extending down to the base of slope, where it spreads out into what appears to be an alluvial fan (Figure 2, pale green stipple unit). A remnant of an even older alluvial ridge or terrace (Figure 2, orange unit) is preserved as an interfluve on the west side of Solly Creek.

Alluvium related to the active drainages is shown by yellow stippled patterns in Figure 2. Solly Creek is the main drainage in the study area. Its upper reaches (above 650 m) are constrained by a steep-sided canyon that has incised through the till and into the underlying bedrock. Upper slopes on the east side of the canyon are covered with colluviated till deposits (Figure 2, pale brown unit). The steeper lower slopes adjacent to the creek are made up of bedrock-derived colluvial veneer overlying bedrock (Figure 2, dark brown unit). Bedrock exposures (too small to be visible at the scale of Figure 2) can be found along the eastern canyon wall, as well as in the streambed itself. Similar colluvial deposits and outcrops are present on the west side of the canyon, but these are capped by unmodified till and the older alluvial gravel ridge mentioned above.

A shallow colluvial veneer over bedrock is also present in the northwestern corner of the study area (medium brown; Figure 2). Two separate areas are mapped, but they could be part of a larger area of bedrock-derived colluvium extending upslope to the northwest. Downslope, the colluvium forms a thin veneer over glacial till.

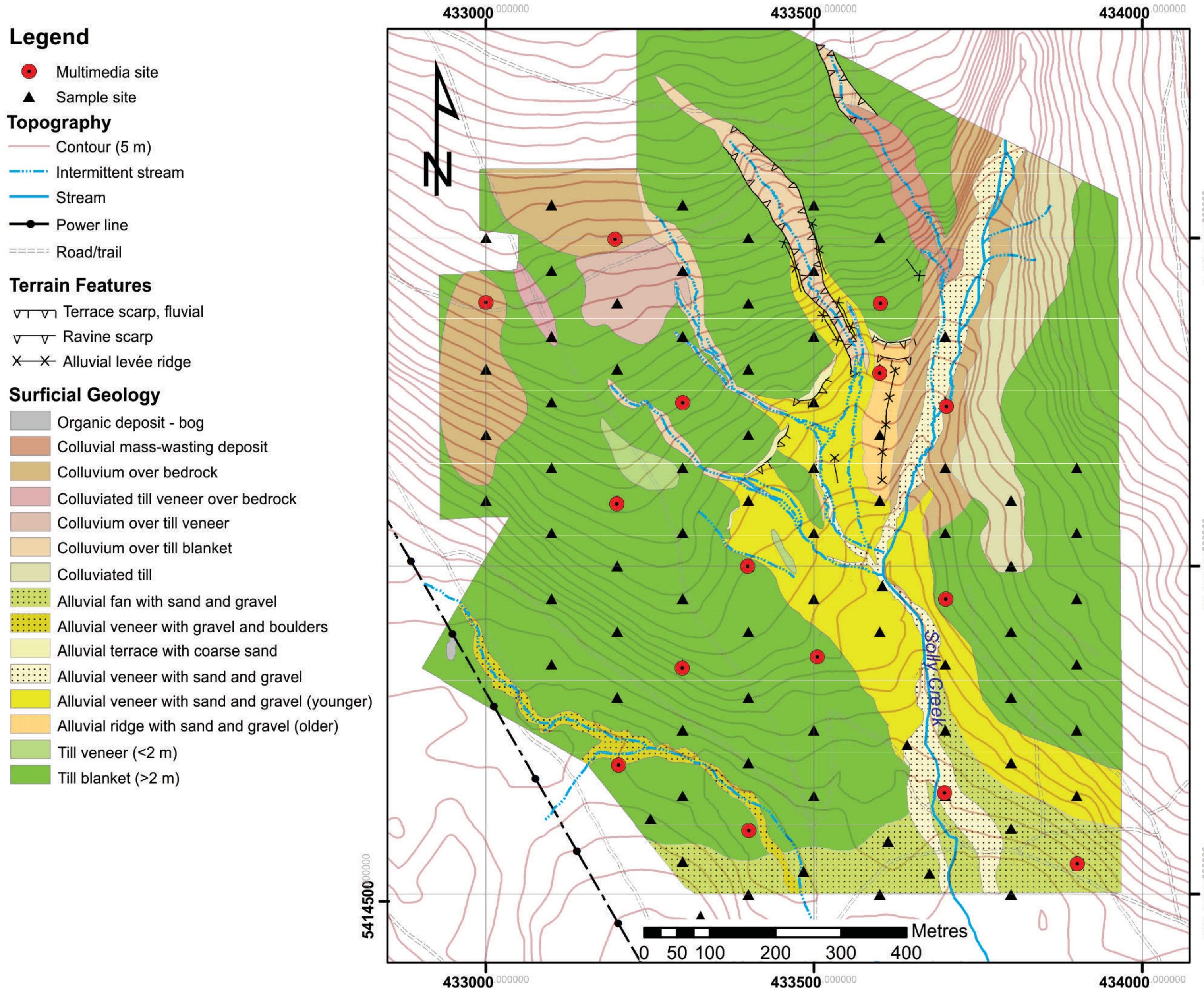

Figure 2. Surficial geology of the Lara study area, east-central Vancouver Island, showing sample stations. Contains information licensed under the Open Government Licence – Canada.

Soil profiles developed on the tills are typical dystric Brunisols. They include a surface LFH layer and an underlying thin Ah horizon lying on top of a generally undifferentiated brown Bm horizon. Iron enrichment at the top of the Bm horizon (Bf horizon) is present at some localities, particularly over alluvial and colluvial deposits. The presence of a discontinuous eluviated horizon (Aej) at some of these localities indicates incipient podzolization over better drained areas.

Geology

The Lara study area is underlain by volcanic and volcaniclastic sedimentary units belonging to the McLaughlin Ridge Formation of the Sicker Group (Massey, 1992; Krocker, 2014). The Sicker Group is known as an important host for Kuroko-type VMS mineralization, the principal economic deposits being the H-W, Lynx, Myra and Price deposits from the Buttle Lake camp (Juras, 1987), located in the Buttle Lake uplift west of Courtenay. Lara lies in a separate uplift, the Cowichan–Horne Lake uplift, in the southern part of the island. Volcanogenic massive-sulphide–style mineralization is hosted by a west-northwest-striking, northeast-dipping package of volcaniclastic sedimentary rocks consisting mostly of sandstone, siltstone, argillite and tuffite (Krocker, 2014). Volcanic rocks are volumetrically subordinate to the volcaniclastic sedimentary rocks. They include aphyric and porphyritic (feldspar, pyroxene and hornblende) rocks, lapilli tuff and breccia of intermediate to mafic composition that lie in the immediate hangingwall to the Coronation trend (Figure 3). Felsic units are relatively common in the Lara area. A narrow quartz-phyric rhyolite-crystal and ash tuff package, known as the Southern Rhyolite sequence, hosts mineralization at the Coronation zone. The unit is intruded by a number of sill-like gabbro bodies. A footwall rhyolite, possibly a dome complex consisting of quartz- and feldspar-phyric rhyolite, has also been identified by a few drillholes in the footwall of the Coronation zone.

South of the Coronation zone, the Sicker Group is abruptly truncated by the Fulford fault, a bedding-subparallel reverse fault that thrusts Sicker Group over younger Nanaimo Group sedimentary units.

Lara mineralization occurs in seven discrete zones (Krocker, 2014). Three of these, the Coronation zone, the Coronation extension and the Hanging wall zone, which together make up the Coronation trend, occur in the area covered by this study. The most important of these is the Coronation zone, which hosts massive, banded/laminated and stringer-style polymetallic sulphide mineralization. The position of these zones, as compiled from historical drilling results, is shown in Figure 3 (Bodnar, pers. comm., 2016). Treasury Metals Inc., holder of the mineral claims to these zones, had reported an indicated-resource estimate (for a 1% Zn block cutoff) of approximately 1 146 700 tonnes averaging 3.01% Zn, 32.97 g/t Ag, 1.05% Cu, 0.58% Pb and 1.97 g/t Au for the Coronation trend, with an additional 669 600 tonnes averaging 2.26% Zn, 32.99 g/t Ag, 0.90% Cu, 0.44% Pb and 1.90 g/t Au of inferred resource (Treasury Metals Inc., 2013). The Coronation trend crosses the southern third of the study area.

Hydrothermal alteration, present mostly in the structural hangingwall east of the Coronation zone, consists of strong pervasive sericitization, defined chemically by Na depletion and K enrichment. It is associated with elevated Zn values and local silicification and disseminated pyrite.

Sampling and Analysis

The aim of the 2016 sampling program was to collect a selection of organic media to test for halogens and other mineralization-related compounds (including NH_4, SO_4 and PO_4). Considerably more samples were collected than could be analyzed under the scope of the project. However, sampling is quick and easy, and it was unknown which medium might provide the most informative response to the concealed mineralization. Therefore, emphasis was placed on collecting the most common species at all sample stations so that samples not initially analyzed would be available for focusing on detailed analysis once initial baseline data were established.

Samples of the dominant tree species (Douglas-fir, western hemlock and western redcedar) were collected from 89 stations arranged in a 100 m spaced offset grid (Figure 4). Ah horizon soils and samples for soil pH and electrical conductivity readings were also collected at these locations. Soil pH and conductivity measurements were done on samples from the top 5 mm of the B horizon. Approximately every fifth sample was designated as a multimedia site, where additional understorey species, including Western sword fern, Oregon-grape and salal, were collected to provide background information on different species. Numbers and types of samples collected are summarized in Table 1 and Figure 4. Limitations on the availability of sample media at some sample stations meant that not all media could be collected at all of the desired sites. This was especially true in areas of ground disturbance caused by road building, mining and drilling activities, as well as in swamps and major drainages.

Twigs and foliage comprising the most recent 5–7 years of growth were collected from each of the dominant tree species. Each sample comprised 5–7 lengths, each of about 25 cm, snipped from around the circumference of a single tree. Samples of outer bark from Douglas-fir and western hemlock were obtained by scraping the scales from around the circumference of neighbouring trees, using a hardened-steel paint scraper, and pouring the scales into a standard ‘Kraft’ paper soil bag (about 50 g, a fairly full bag).

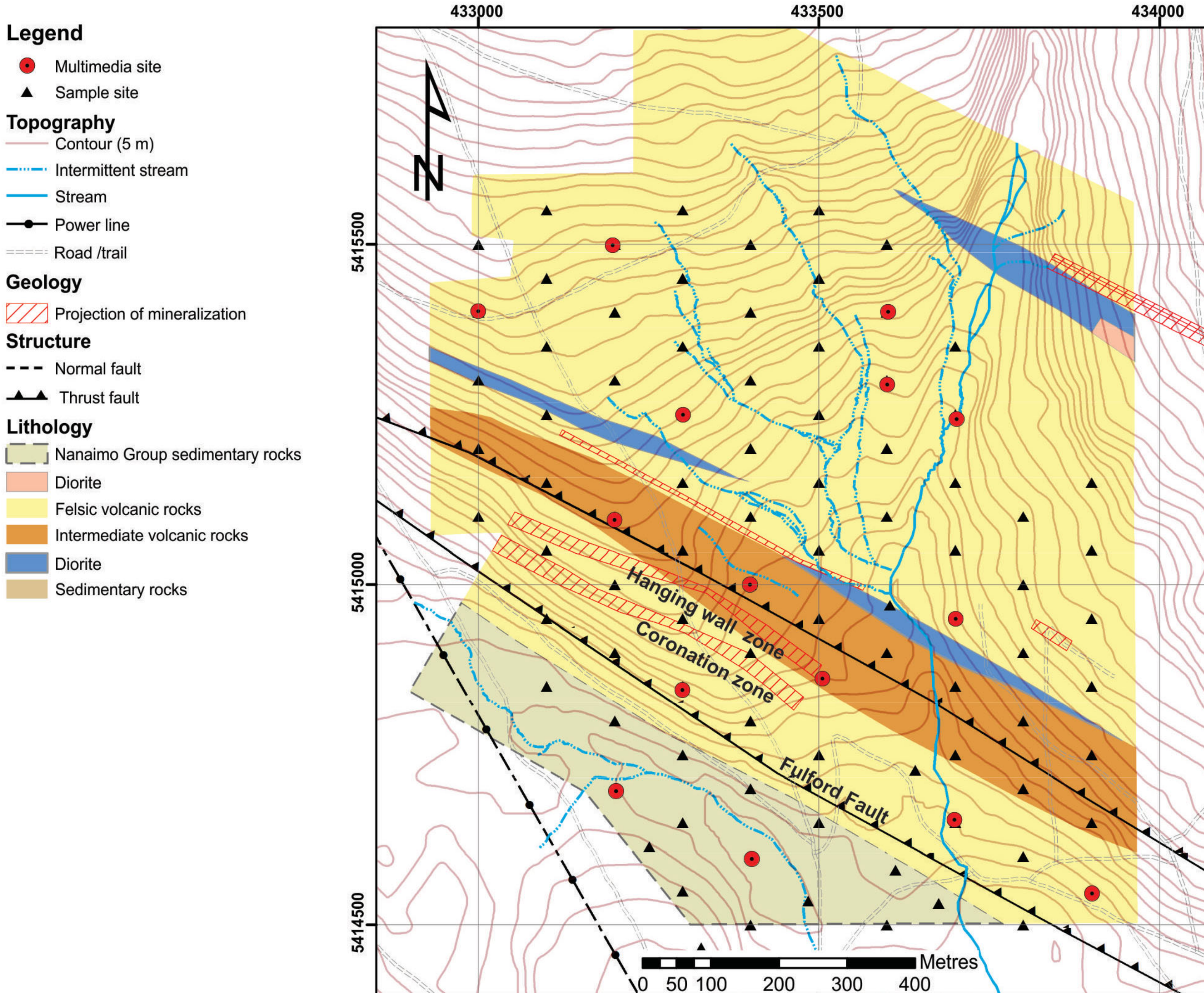

Figure 3. Geology of the Lara study area, east-central Vancouver Island, showing surface projections of the mineralized horizons (red hatching). Contains information licensed under the Open Government Licence – Canada.

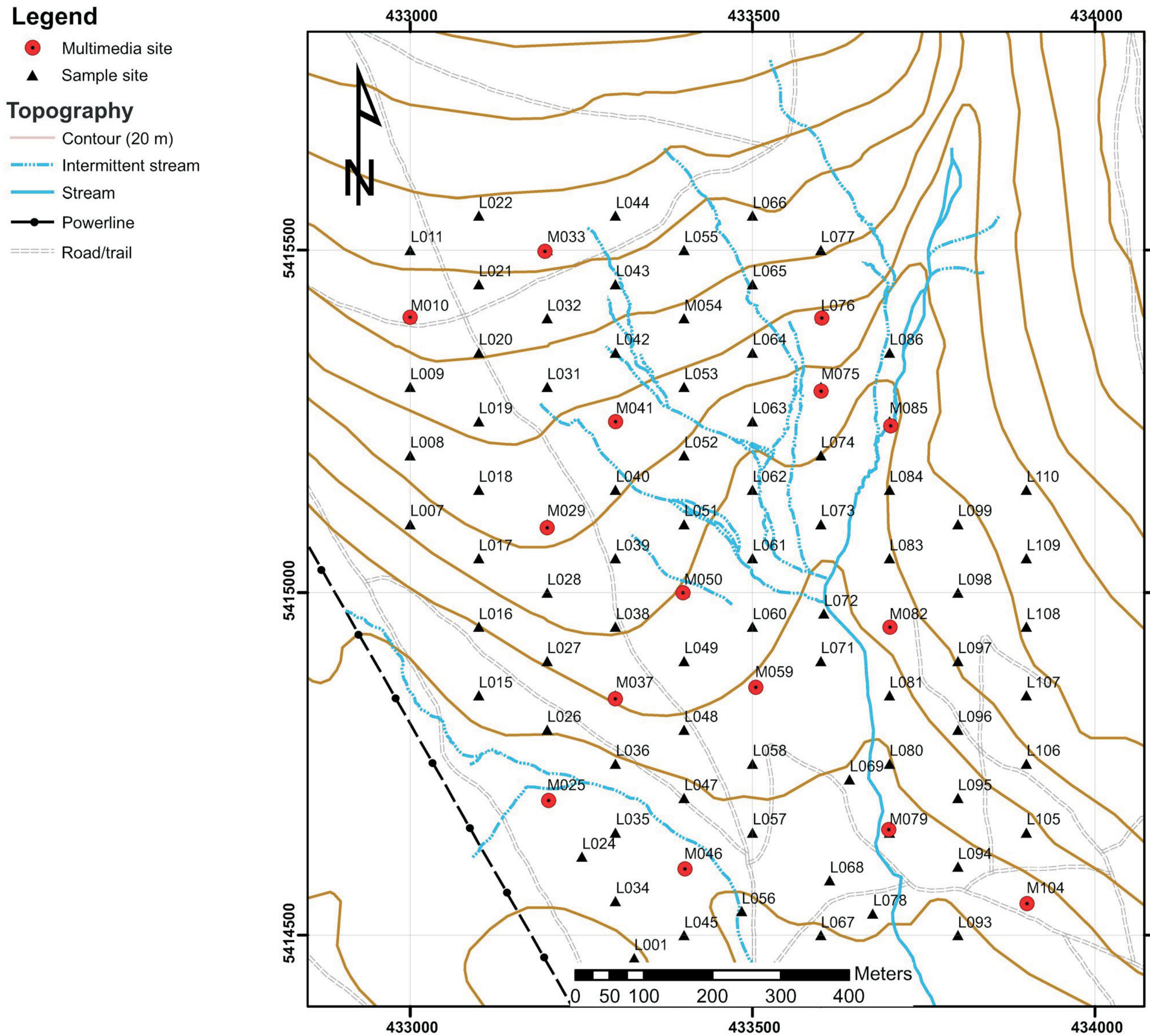

Figure 4. Locations of samples in the Lara study area, east-central Vancouver Island. Contains information licensed under the Open Government Licence – Canada.

Table 1. Numbers and types of samples collected in the Lara study area, east-central Vancouver Island.

Sample medium	No. of samples
Western hemlock foliage (WHF)	89
Douglas-fir bark (DFB)	79
Western redcedar foliage (RCF)	89
Western hemlock bark (WHB)	68
Salal foliage (SALF)	17
Western Sword fern foliage (SF)	8
Oregon-grape foliage (OGF)	8
Ah horizon soil	88
Soil pH & electrical conductivity	81

Foliage from the understorey species collected at the multi-media sites was sampled by gripping a stem near the base and pulling upward to strip off the leaves. Leaves were collected from two or three plants and placed in a 13 by 9 inch Hubco New Sentry® fabric sample bag.

Vegetation and soil samples were oven dried at 80° C for 24 hours to remove all moisture. Ah horizon soil samples were sieved to –80 mesh (177 µm) in preparation for analysis of the finer fraction. Foliage was separated from twigs. All foliage and bark samples were then milled to a fine powder. Each sample medium was split into either two or three subsets for submission to several laboratories for different treatments (Table 2). This table is a work in progress that will be refined once experimental work has been completed

Initially, a split of each sample of western hemlock needles was subjected to a warm-water leach in accord with the method developed by G. Hall (Dunn et al., 2007):

> *"Soil and vegetation samples were leached by placing a 1 g sample in 10 mL deionized water which was then vortexed and allowed to sit for 1 hour at 30°C in an incubator. Samples were then centrifuged and filtered through a 0.45 micron filter."*

Leachates from approximately 200 vegetation samples were analyzed by high-performance liquid chromatography–ion chromatography (HPLC-IC) for Cl, Br, I, PO_4 and SO_4. The same solutions were analyzed on an AutoAnalyzer (an automated analyzer using continuous-flow analysis [CFA]), for nitrate (NO_3) and ammonium (NH_4), and for fluoride ($F^–$) using an ion-selective electrode (ISE) and ion chromatography. Separate splits of the milled western hemlock needles and sieved Ah soils were sent to Activation Laboratories Ltd. ('Actlabs'; Ancaster, ON) for analysis by their proprietary Bioleach method. Actlabs states that:

> *"It has been proven that microbiological processes [in the subsurface] are exceptionally important. Electrochemical Redox cells mobilize metals from the mineral deposit to the surface which become adsorbed on soil particles and create unique surficial conditions that bacteria then feed upon. Bioleach digests bacteria and their proteins from the collected surficial samples to analyze for the elements related to the blind mineralization. A 0.75 g sample is leached in a proprietary matrix at 30°C for 1 hour, and the solutions are analyzed on a Perkin Elmer ELAN 6000, 6100 or 9000 ICP/MS."*

Quality Control

Quality-control measures employed in the Lara study include collection of field-duplicate samples for each sample type, as well as insertion of 'blind' control samples (milled vegetation of similar matrix and known composition) for the vegetation and Ah horizon samples. Table 3 summarizes the control samples employed.

Results

The only data received by the time of writing were:

1) Ah soils and Western hemlock foliage by Bioleach; completed and excellent precision for almost all elements, including Br and I
2) Ah soils by aqua regia
3) preliminary numbers for NO_3 and NH_4 from the AutoAnalyzer and $F^–$ by ISE, with an updated analytical report expected in the near future; moderate variability in the and is reported, and there are unusually high concentrations of $F^–$ in all eight of the sword fern samples collected

Table 2. Summary of analytical methods used for samples from the Lara study area, east-central Vancouver Island.

Sample media[1]	Laboratory	Digestion	Analytical methods
Ah horizon – all sites	ALS Minerals, North Vancouver, BC	Aqua regia	ME-ICP41L
Ah horizon – all sites	ALS Minerals, North Vancouver, BC	Warm water leach	ME-MS14L including all halogens
Ah horizon – all sites	Actlabs, Ancaster, ON	Bioleach	ICP-MS
WHF – all sites	Actlabs, Ancaster, ON	Bioleach	ICP-MS
WHF - all sites	BC MOE Laboratory, Victoria, BC	Warm H_2O	HPLC-IC for Cl, Br, I, PO_4 and SO_4; F by ISE
WHB, RCF, SAL, SF, OGF	BC MOE Laboratory, Victoria, BC	Warm H_2O	ICP-MS
WHF, WHB, RCF, SAL, SF, OGF	BC MOE Laboratory, Victoria, BC	Microwave HNO_3	ICP-MS
WHB, RCF, SAL, SF, OGF	ALS Minerals, North Vancouver, BC	Warm H_2O	ME-MS14L including all halogens

[1]See Table 1 for abbreviation definitions

Abbreviations: BC MOE, BC Ministry of Environment (Environmental Sustainability and Strategic Policy Division, Knowledge Management Branch); HPLC-IC, high-performance liquid chromatography–ion chromatography; ISE, ion-selective electrode

Table 3. Summary of quality-control samples used in the Lara study, east-central Vancouver Island.

Sample medium	No. of samples	Standards		Field duplicates
		V14	LIM-2011	
Western redcedar foliage (RCF)	90	2		8
Western hemlock foliage (WHF)	89	9		8
Douglas-fir bark (DFB)	79	2		7
Western hemlock bark (WHB)	68	9		2
Salal foliage (SALF)	17	2		0
Western sword fern foliage (SF)	8	1		0
Oregon-grape foliage (OGF)	8	1		0
Ah horizon	88	8	9	8

Analytical development work will be ongoing through the fourth quarter of 2016. Interpretation of the analytical results and preparation of the final report will be completed following the snow-sampling program in January 2017.

Acknowledgments

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